Supporting Information

On the mechanism of intramolecular sensitization of photocleavage of the 2-(2-nitrophenyl)propoxycarbonyl (NPPOC) protecting group

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1. CCD spectra and decay curves

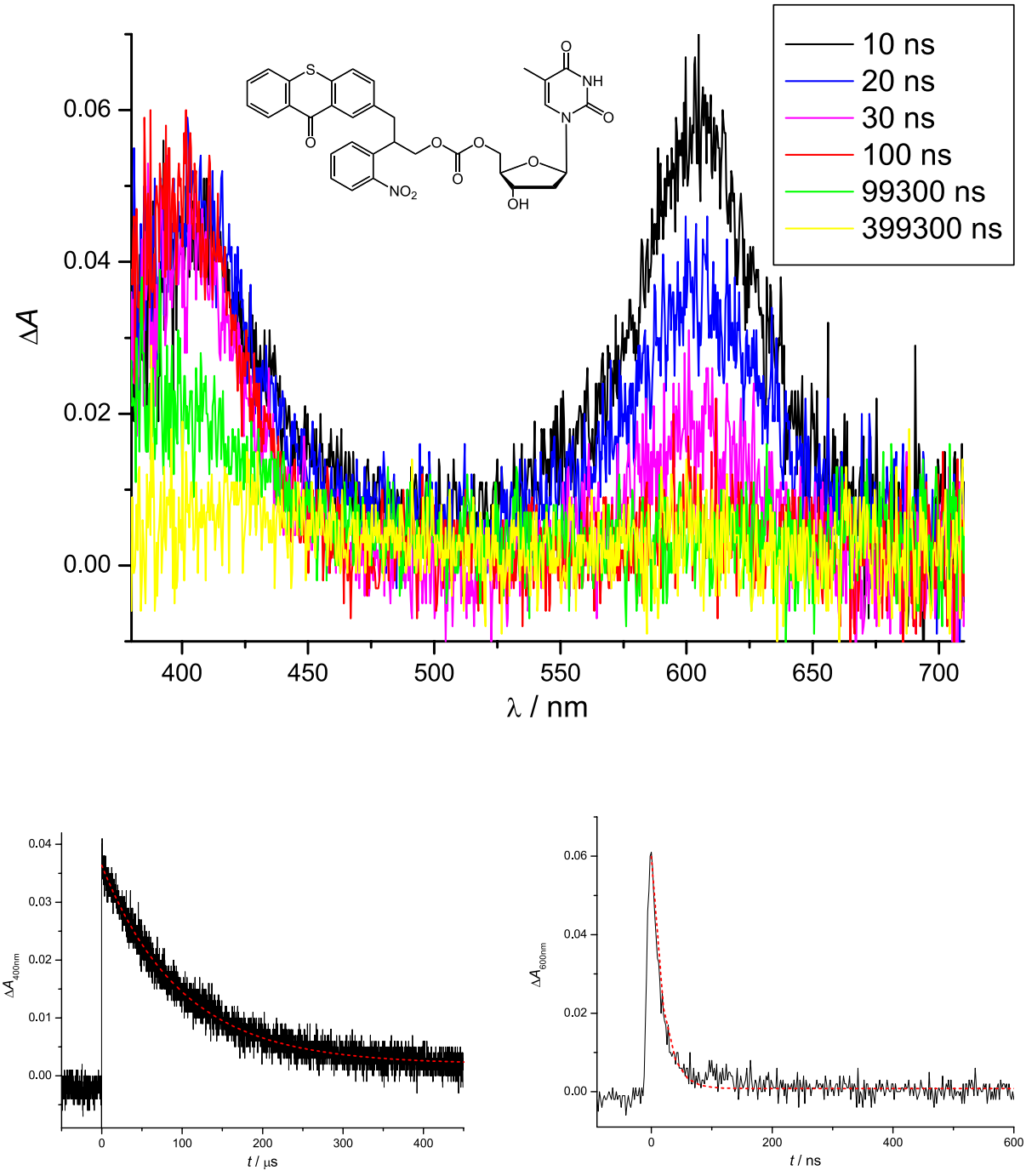


Figure S1: Laser flash spectra and decaying curves (at 400 nm and 600 nm) of T7S2-O(CO)Thy in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

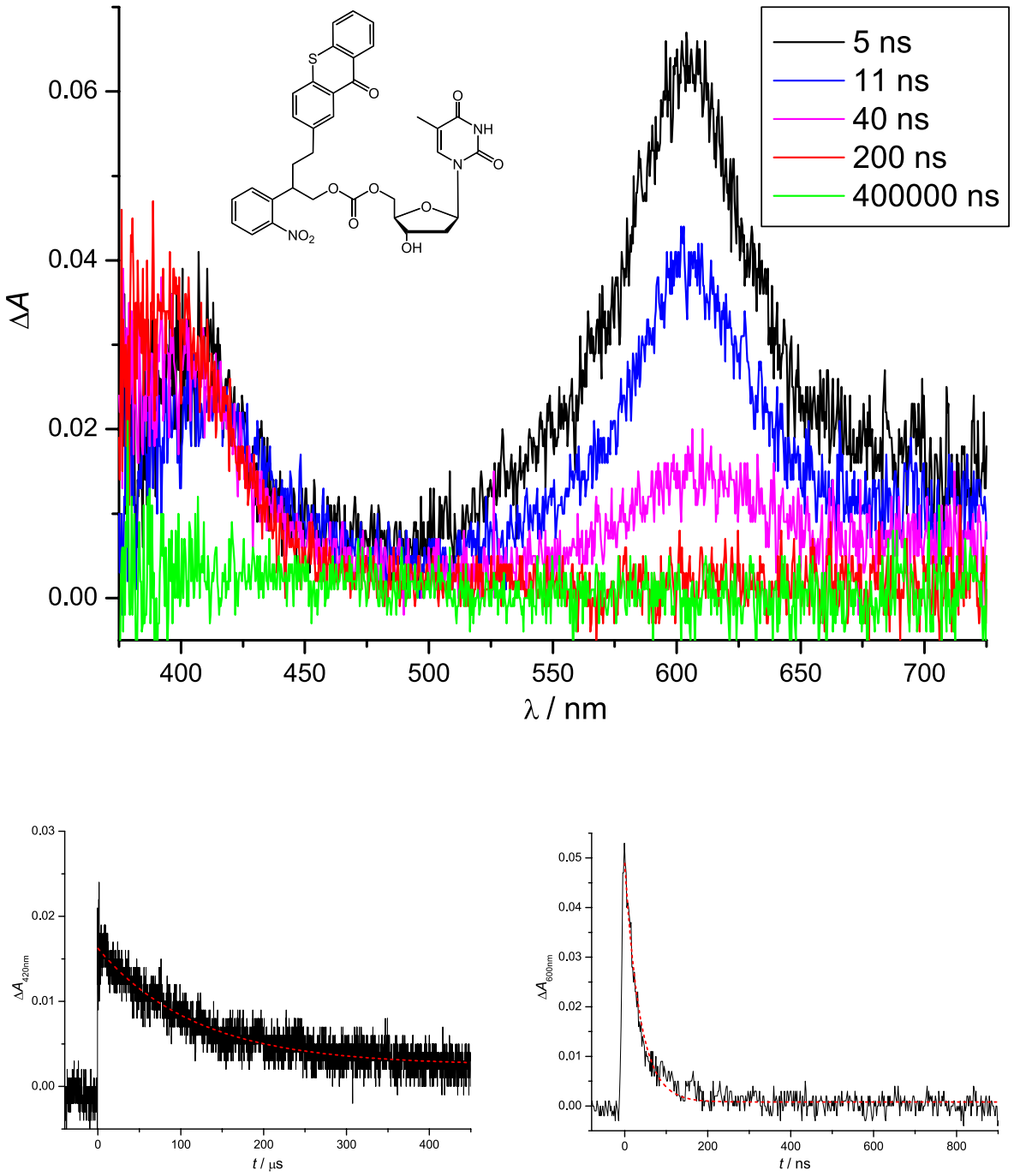


Figure S2: Laser flash spectra and decaying curves (at 420 nm and 600 nm) of T7S3-O(CO)Thy in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

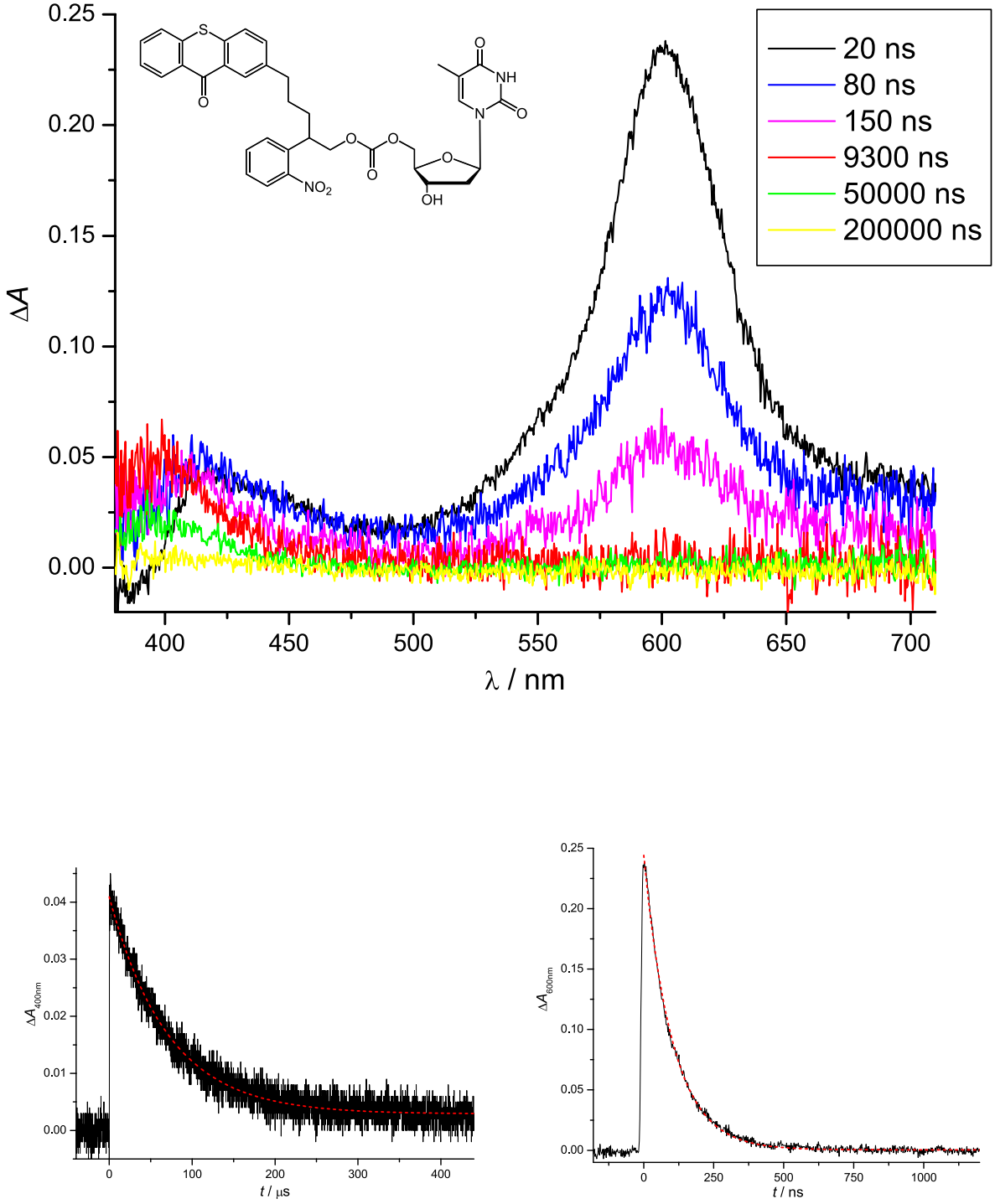


Figure S3: Laser flash spectra and decaying curves (at 400 nm and 600 nm) of T7S4-O(CO)Thy in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

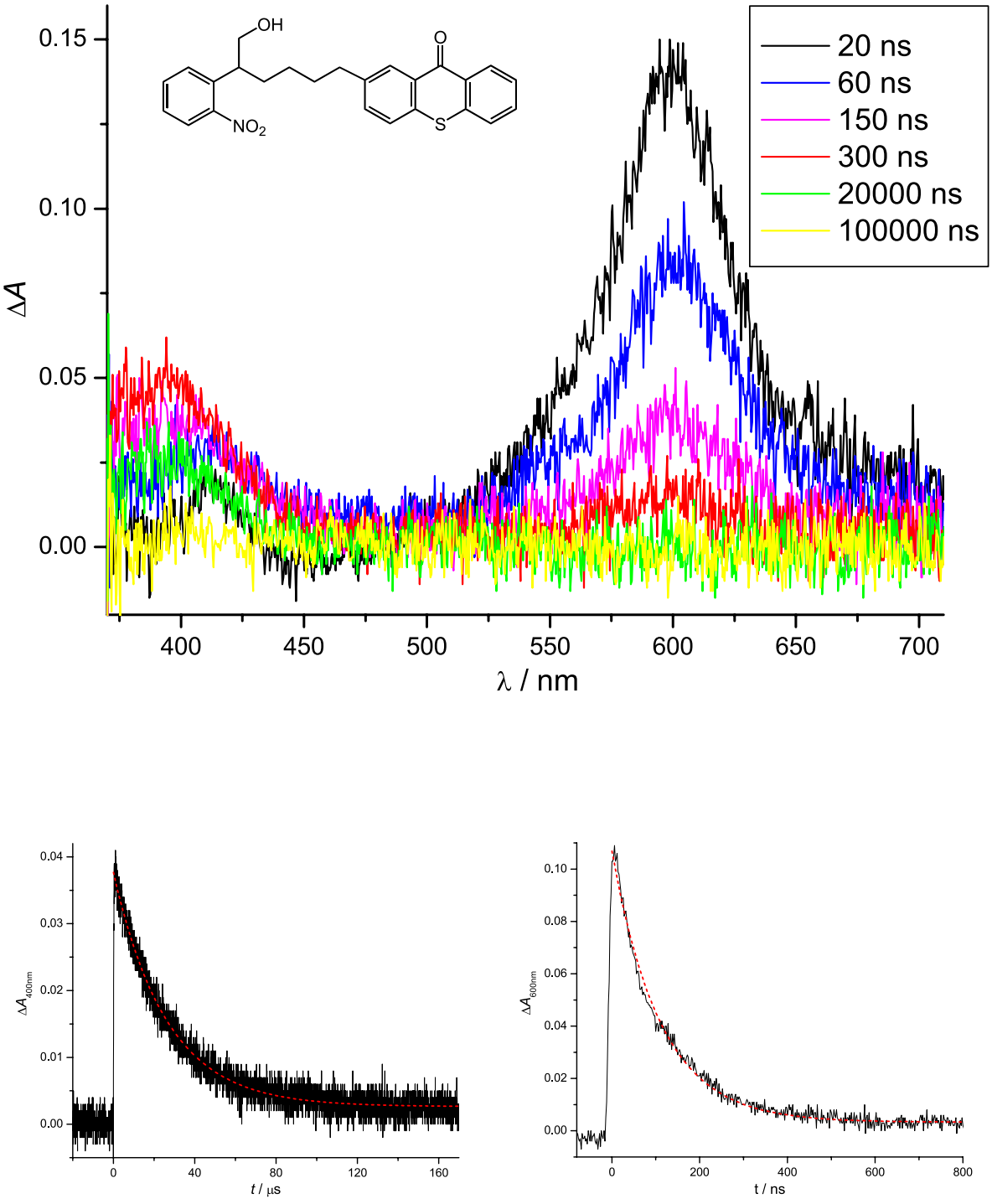


Figure S4: Laser flash spectra and decaying curves (at 400 nm and 600 nm) of T7S5-OH in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

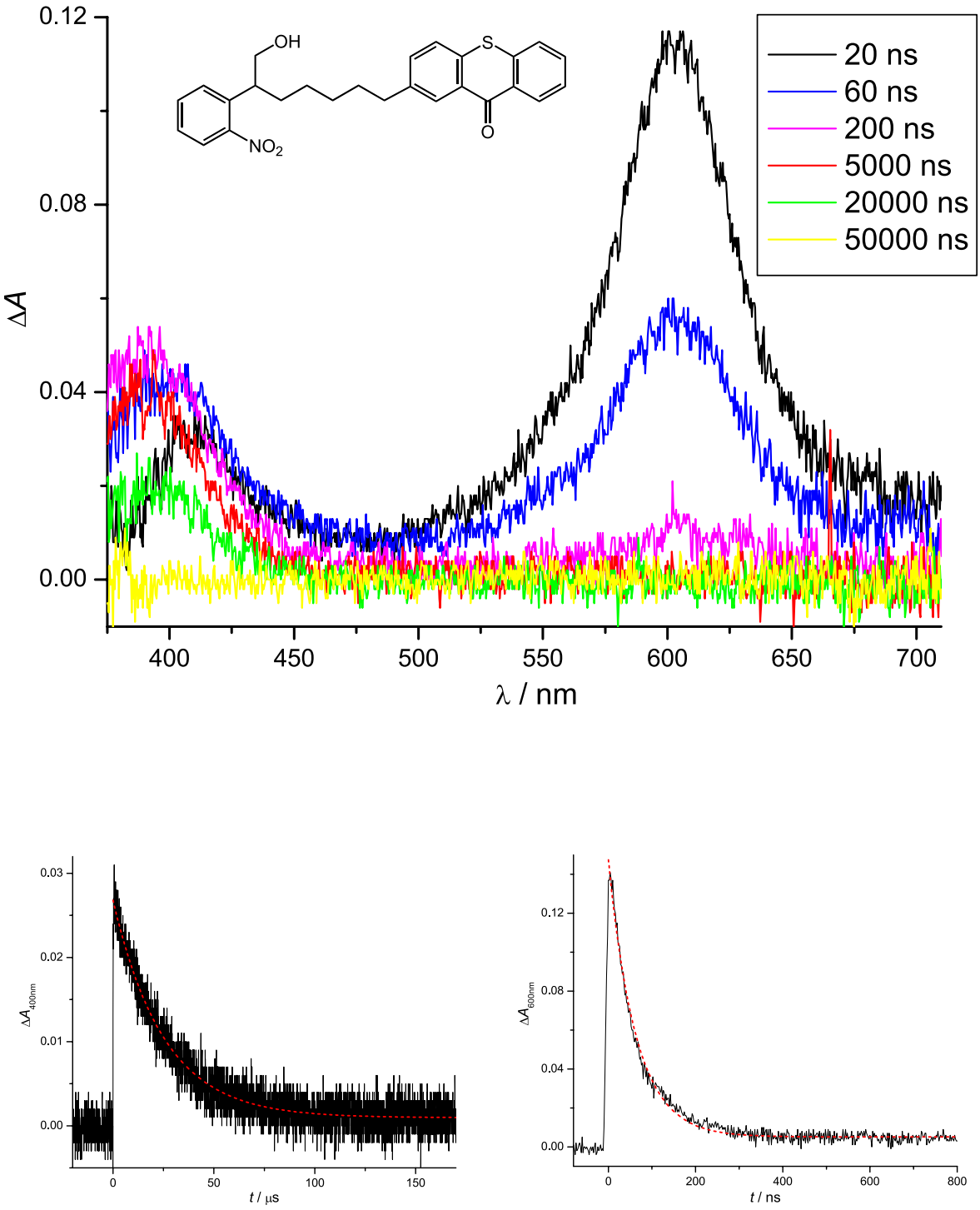


Figure S5: Laser flash spectra and decaying curves (at 400 nm and 600 nm) of T7S6-OH in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

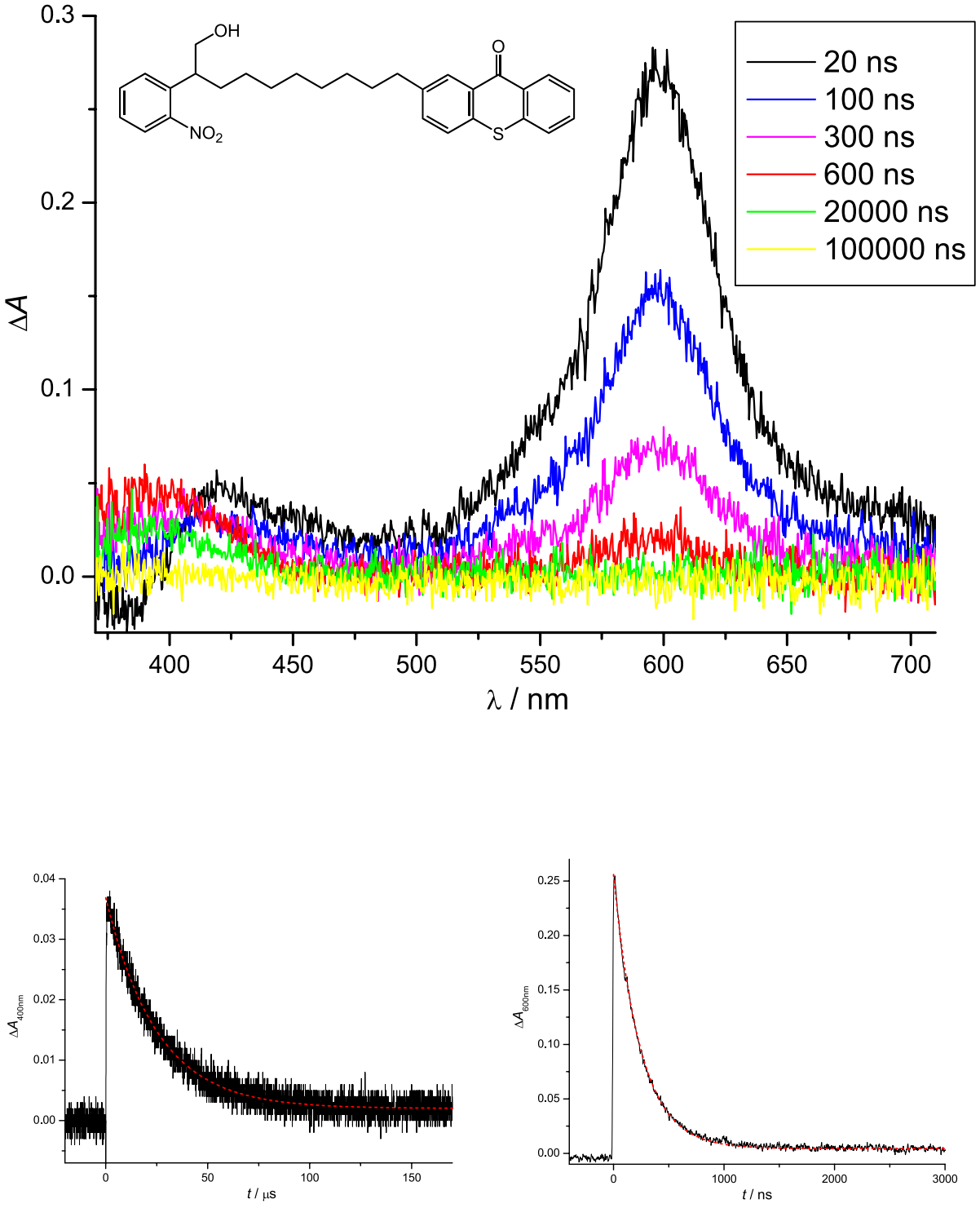


Figure S6: Laser flash spectra and decaying curves (at 400 nm and 600 nm) of T7S9-OH in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

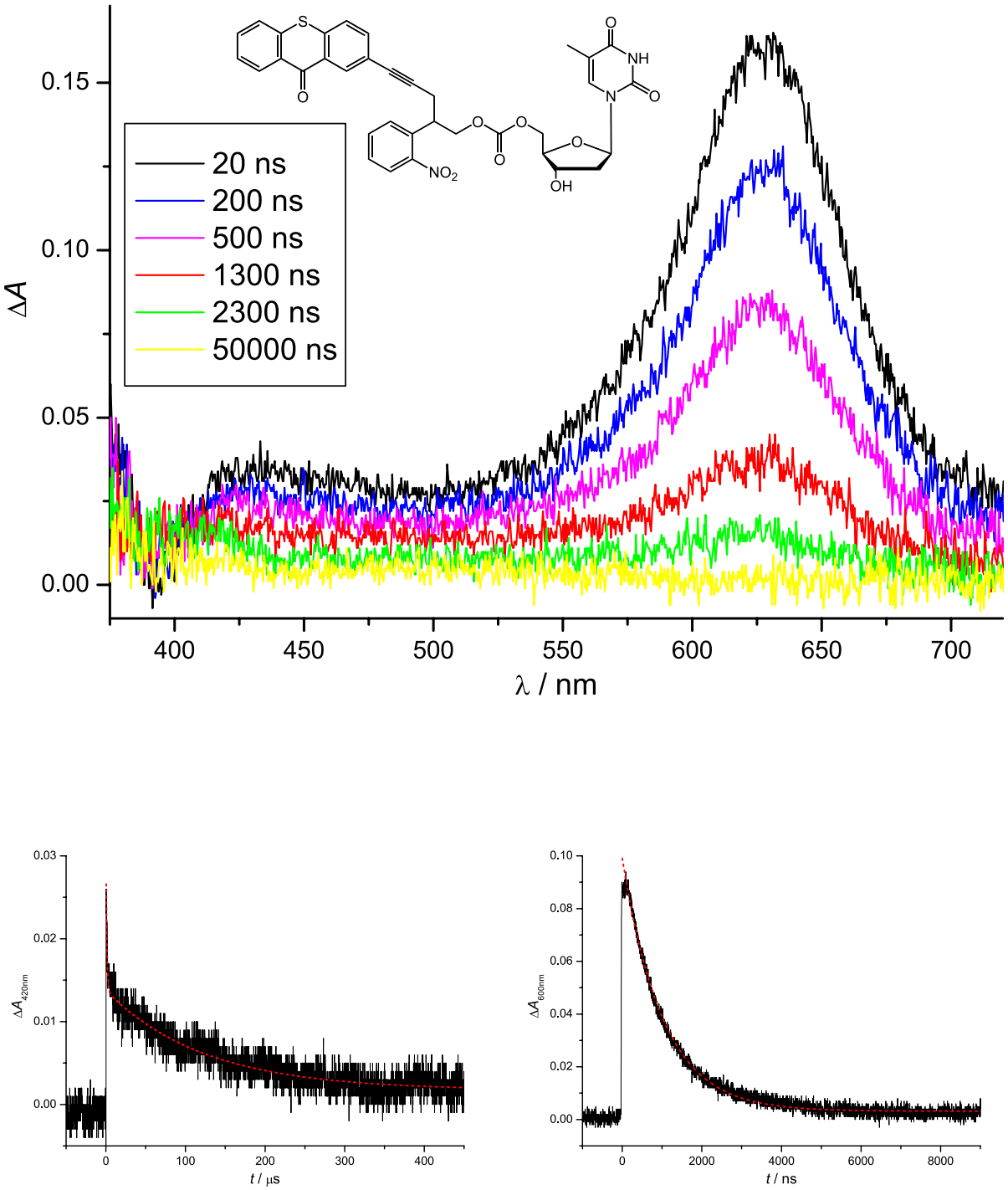


Figure S7: Laser flash spectra and decaying curves (at 420 nm and 600 nm) of T7T4-O(CO)Thy in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

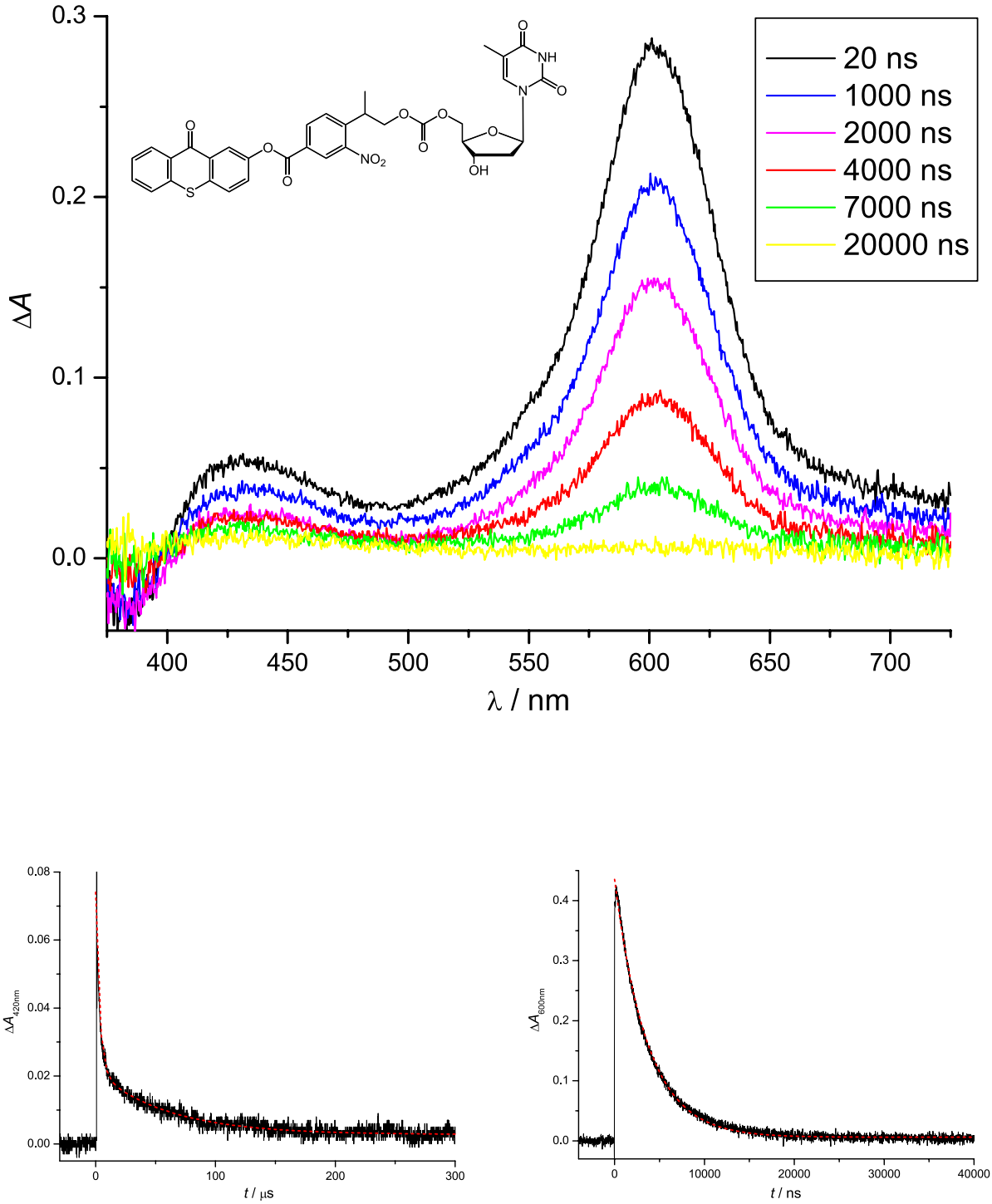


Figure S8: Laser flash spectra and decaying curves (at 420 nm and 600 nm) of T4E2-O(CO)Thy in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

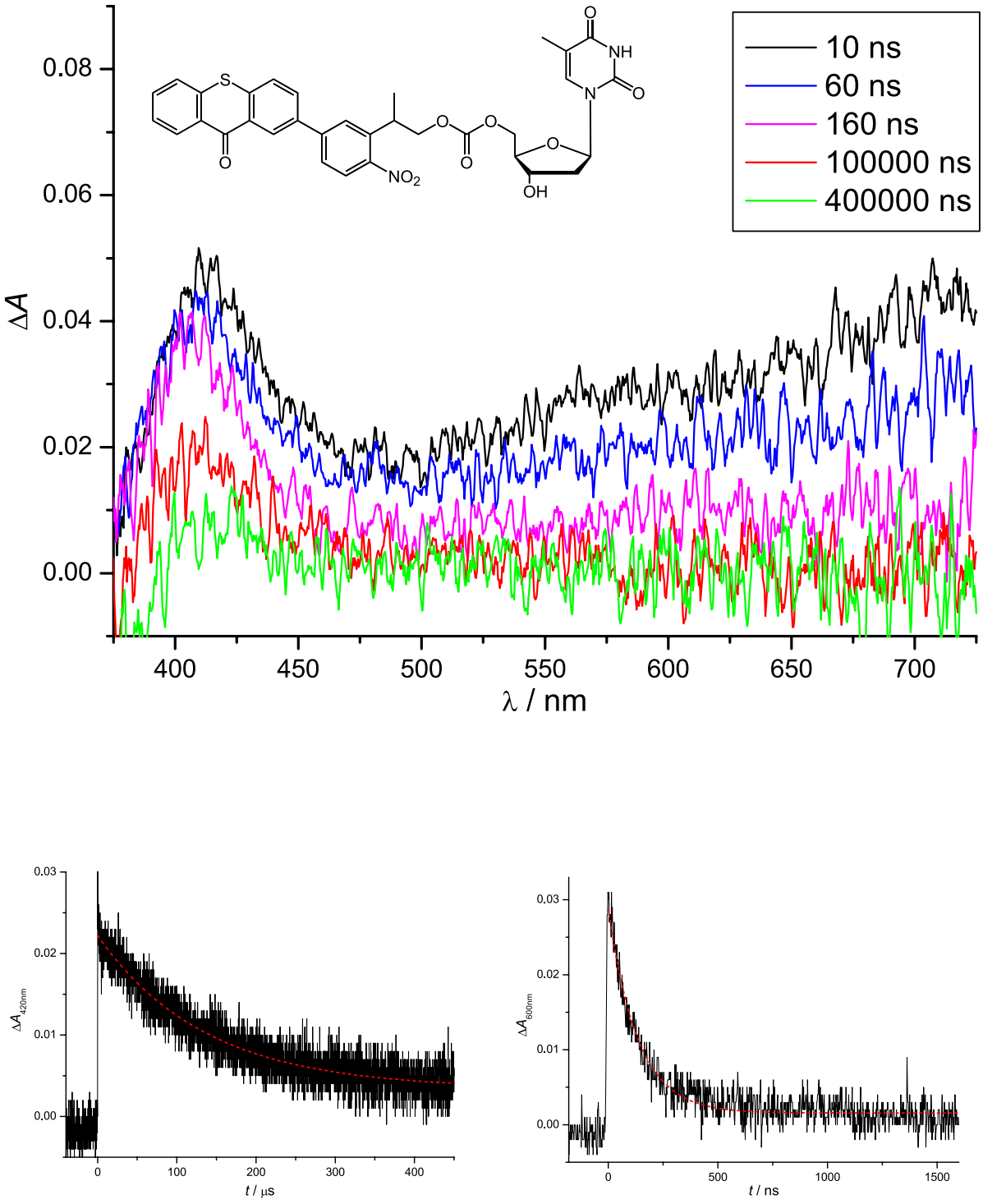


Figure S9: Laser flash spectra and decaying curves (at 420 nm and 600 nm) of T5S0-O(CO)Thy in nitrogen saturated MeOH. Solutions were adjusted to an absorbance of 0.215 at 355 nm, the excitation wavelength.

2. Estimation of energy of charge transfer state $[TX]^-[NPPOC]^+$

The following equation was used to estimate the standard Gibbs energy change ΔG^{e}_{ESCT} of the excited state charge transfer reaction A*..D $\rightarrow$ $A^-..D^+$ for (excited) acceptor A and donor D separated by a distance *a*:

$$\Delta G^{e}_{ESCT} = F(E^{e}_{D/D^+} - E^{e}_{A/A^-}) - \frac{e_0^2}{4\pi\varepsilon\varepsilon_0 a} - E(A^*)$$

Here E^{e}_{D/D^+} and E^{e}_{A/A^-} are the standard oxidation and reduction potentials of D and A, respectively, $E(A^*)$ is the electronic energy of the excited acceptor. The electrical constants *F*, e_0, ε and ε_0 have their usual meanings. The following values were used: E^{e}_{TX/TX^-} = -1,24 V,[a] $E(^1TX^*)$ = 2,96 eV,[b] $E^{e}_{NPPOC/NPPOC+}$ = 1,39 V.[c] Assuming 7 Å, an often used value for the distance *a* of an exergonic outer sphere electron transfer, we obtain ΔG^{e}_{ESCT} = - 0,39 eV (-37.6 kJ/mol).

[a] A value of -1.97 V vs Ag/0.1 M Ag^+, which has a potential of 0.732 V vs NHE, was reported for the standard reduction potential of TX by Tsai et al.[1]

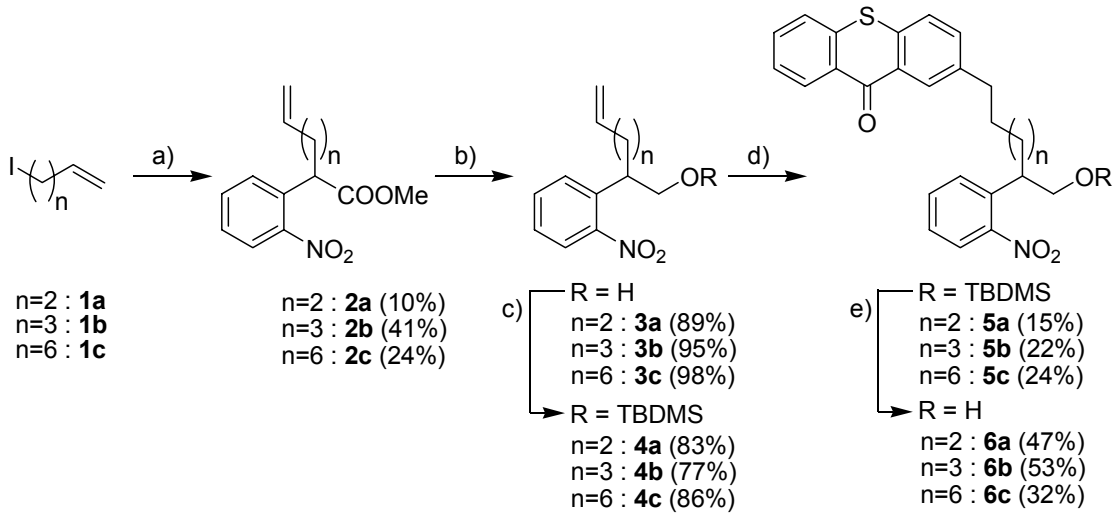
[b] This value is based on a wavelength of 420 nm for the onset of the first absorption band.

[c] The oxidation potential of NPPOC was assumed to be equal to the oxidation potential of nitrobenzene, which is probably an upper limit for NPPOC. The oxidation potential of nitrobenzene was reported to be 1,6 V vs. an Ag/AgCl, KCl (3 M) reference electrode.[2] The latter's potential vs. NHE is 0.210 V.[3]

3. Syntheses

The compounds T7S*n*-OH (*n* =2, 5, 6, 9), T7S2-O(CO)Thy, TOBz and T5S0-M were synthesized as follows. We note that the reactions have not been optimized.

Synthesis of **2a**, **2b**, **2c**. Methyl (2-nitrophenyl)acetate (4.46 g, 22.9 mmol, 1 eq.) and the alkenyl iodide (22.9 mmol, 1 eq.) were dissolved in THF (30 mL) under N_2-atmosphere. KO^{t}Bu (24.9 mmol, 1.1 eq.) was added at -78°C. The blue suspension was left to warm to r.t. and stirred for 2 d. It was cooled to -78°C and sat. NH_4Cl-solution was added resulting in disappearance of the blue color. At r.t. CH_2Cl_2 (30 mL) was added and the organic phase separated (2 × with CH_2Cl_2), washed by water and dried over $MgSO_4$. The solvent was evaporated and the residue subjected to column chromatography (silica gel, petrol ether-EtOAc-gradient).



Scheme S1: a) Methyl(2-nitrophenyl)acetate, KO^{t}Bu, THF, -78°C → r.t., 2 d; b) $NaBH_4$, THF, MeOH, r.t., 3 h; c) TBDMS-Cl, imidazole, CH_2Cl_2, 0°C → r.t., 24 h; d) 9-BBN, THF, r.t., then 2-bromothio-xanthone, Pd(dppf)Cl_2, 3M aq. K_3PO_4, DMF, 80°, 4 h; (e) Bu_4NF, THF, 0°C → r.t., 12 h.

2a: yellow oil; 10% yield; ^{1}H–NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.60–7.51 (m, 2H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 5.76 (ddt, *J* = 17.6, 9.8, 6.6 Hz, 1H, =C*H*), 5.01–4.95 (m, 2H, CH_2), 4.19 (t, *J* = 7.0 Hz, 1H), 3.66 (s, 3H, Me), 2.32–2.22 (m, 1H), 2.09–2.02 (m, 2H), 1.97–1.88 (m, 1H).

2b: yellow oil; 41% yield; ^{1}H–NMR (400 MHz, $CDCl_3$): δ 7.85 (dd, *J* = 8.2, 1.3 Hz, 1H, *H*–C(3)), 7.60–7.51 (m, 2H), 7.40 (td, *J* = 6.9, 1.7 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H, =C*H*), 5.01–4.91 (m, 2H, CH_2), 4.17 (t, *J* = 7.4 Hz, 1H), 3.65 (s, 3H, Me), 2.20–2.10 (m, 1H), 2.09–2.02 (m, 2H), 1.88–1.78 (m, 1H), 1.50–1.28 (m, 2H).

2c: yellow oil; 24% yield; ^{1}H–NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.60–7.51 (m, 2H), 7.43–7.37 (m, 1H), 5.77 (ddt, *J* = 17.0, 10.1, 6.7 Hz, 1H, =C*H*), 5.00–4.88 (m, 2H, CH_2), 4.16 (t, *J* = 7.3 Hz, 1H), 3.66 (s, 3H, Me), 2.17–2.10 (m, 1H), 2.03–1.97 (m, 2H), 1.85–1.76 (m, 1H), 1.40–1.19 (m, 9H).

Synthesis of **3a**, **3b**, **3c**. The ester **2** (37.4 mmol, 1 eq.) and $NaBH_4$ (232 mmol, 6.2 eq.) were suspended in THF (100 ml) under N_2-atmosphere and MeOH (20 ml) was slowly added during 3 h at r.t. After stirring overnight, H_2O (10 ml) was added and the volume of the solution was reduced to 20% of the initial volume. After the extraction with CH_2Cl_2 (3 × 50 ml) the combined organic phase was washed with H_2O, dried over $MgSO_4$ and the solvent evaporated. The product could be used for the next step without further purification.

3a: yellow oil; 89% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 7.76 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.65 (td, *J* = 7.6, 1.2 Hz, 1H, *H*–C(5)), 7.59 (dd, *J* = 8.1, 1.5 Hz, 1H, *H*–C(6)), 7.43 (td, *J* = 7.6, 1.5 Hz, 1H, *H*–C(4)), 5.73 (ddt, *J* = 16.9, 10.5, 6.7 Hz, 1H, =C*H*), 4.94–4.88 (m, 2H, =CH_2), 4.75 (t, *J* = 5.3 Hz, 1H, O*H*), 3.62–3.50 (m, 2H, CH_2OH), 3.13–3.06 (m, 1H), 1.93–1.83 (m, 2H), 1.74–1.65 (m, 1H).

3b: yellow oil; 95% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 7.74 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.63 (td, *J* = 7.5, 1.2 Hz, 1H, *H*–C(5)), 7.57 (dd, *J* = 7.8, 1.5 Hz, 1H, *H*–C(6)), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H, *H*–C(4)), 5.73 (ddt, *J* = 16.9, 10.3, 6.8 Hz, 1H, =C*H*), 4.97–4.89 (m, 2H, =CH_2), 4.71 (t, *J* = 5.4 Hz, 1H, O*H*), 3.57–3.47 (m, 2H, CH_2OH), 3.11–3.03 (m, 1H), 2.02–1.92 (m, 2H), 1.83–1.74 (m, 1H), 1.63–1.53 (m, 1H), 1.31–1.11 (m, 2H).

3c: yellow oil; 98% yield; used without further characterization.

Synthesis of **4a**, **4b**, **4c**. TBDMS-Cl (39 mmol, 1.1 eq) and imidazole (44 mmol, 1.3 eq) were added to a solution of the alcohol (35 mmol, 1 eq.) in dry CH_2Cl_2 (150 ml) at 0°C under stirring. This resulted in a colorless precipitate. The suspension was stirred at r.t. for 24 h. MeOH (20 ml) was added and the colorless precipitate dissolved. Stirring was continued for 10 min followed by addition of sat. $NaHCO_3$ solution (100 ml). The organic phase was separated and the remaining water phase re-extracted with CH_2Cl_2 (3 × 30 ml). The unified organic phase was washed with saturated $NaHCO_3$-solution, dried over $MgSO_4$ and the solvent evaporated. After column chromatography (silica gel, petrol ether-EtOAc-gradient) the product was obtained.

4a: yellow oil; 83% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 7.77 (dd, *J* = 8.2, 1.1 Hz, 1H, *H*-C(3)), 7.68–7.60 (m, 2H, *H*-C(5) and *H*-C(6)), 7.44 (td, *J* = 7.4, 1.7 Hz, 1H, *H*-C(4)), 5.74 (ddt, *J* = 16.9, 10.7, 6.4 Hz, 1H, =C*H*), 4.95–4.89 (m, 2H, =CH_2), 3.75 (dd, *J* = 10.0, 5.9 Hz, 1H, C*H*H'O), 3.65 (dd, *J* = 10.0, 7.1 Hz, 1H, CH*H'*O), 3.22–3.15 (m, 1H), 1.94–1.82 (m, 3H), 1.78–1.69 (m, 1H), 0.76 (s, 9H, ^{t}Bu), -0.10 (s, 3H, Si–CH_3), -0.12 (s, 3H, Si–CH_3).

4b: yellow oil; 77% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 7.76 (dd, *J* = 8.2, 1.3 Hz, 1H, *H*–C(3)), 7.67–7.58 (m, 2H, *H*–C(5) und *H*–C(6)), 7.44 (td, *J* = 7.6, 1.5 Hz, 1H, *H*–C(4)), 5.73 (ddt, *J* = 17.1, 10.8, 6.6 Hz, 1H, =C*H*), 4.98–4.89 (m, 2H, =CH_2), 3.73 (dd, *J* = 9.9, 5.7 Hz, 1H, C*H*H'O), 3.65 (dd, *J* = 10.0, 7.3 Hz, 1H, CH*H'*O), 3.20–3.12 (m, 1H), 2.01–1.95 (m, 2H, CH_2CH=), 1.81–1.72 (m, 1H), 1.68–1.58 (m, 1H), 1.33–1.14 (m, 2H), 0.75 (s, 9H, ^{t}Bu), -0.10 (s, 3H, Si–CH_3), -0.13 (s, 3H, Si–CH_3).

4c: yellow oil; 86% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 7.75 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.67–7.58 (m, 2H, *H*–C(5) und *H*–C(6)), 7.43 (td, *J* = 7.5, 1.4 Hz, 1H, *H*–C(4)), 5.76 (ddt, *J* = 17.1, 10.3, 6.6 Hz, 1H, =C*H*), 5.00–4.89 (m, 2H, =CH_2), 3.73 (dd, *J* = 9.9, 5.7 Hz, 1H, C*H*H'O), 3.65 (dd, *J* = 9.8, 7.3 Hz, 1H, CH*H'*O), 3.18–3.11 (m, 1H), 1.97 (q, *J* = 7.0 Hz, CH_2CH=), 1.80–1.70 (m, 1H), 1.67–1.57 (m, 1H), 1.32–1.05 (m, 8H), 0.75 (s, 9H, ^{t}Bu), -0.10 (s, 3H, Si–CH_3), -0.13 (s, 3H, Si–CH_3).

Synthesis of **5a**, **5b**, **5c**. 9-Borabicyclo[3.3.1]nonan (9-BBN, 0.5 M in THF, 60 ml, 30 mmol, 1.3 eq.) was slowly (during a period of 1 h) added to a solution of the TBDMS-protected alcohol **4a** - **4c** (20.8 mmol, 1 eq.) in dry THF (15 ml) under N_2-atmosphere. The solution was stirred until no reactant could be detected by TLC. In another flask, 3M aq. K_3PO_4-solution (8 ml, 24 mmol, 1.1 eq.) and DMF (60 ml) were added to Pd(dppf)Cl_2 (500 mg, 0.68 mmol, 0.03 eq.), and the mixture was vigorously stirred for 15 min. 2-Bromothioxanthone (6.3 g, 21.6 mmol, 1 eq.) and the solution of the synthesized boran (see above) were admixed to the resulting dark-red solution which was then stirred for 4 h at 80°C. After cooling, Et_2O (150 ml) and sat. NaCl-solution (100 ml) were added. The organic layer was separated and the aq. phase re-extracted with Et_2O (3 × 30 ml). The unified organic phase was washed with sat. $NaHCO_3$-solution (50 ml), dried over $MgSO_4$ and the solvent evaporated. The clean product was obtained after column chromatography (silica gel, petrol ether-EtOAc-gradient).

5a: yellow oil; 15% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.46 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–(8)(Tx)), 8.25 (d, *J* = 1.8 Hz, 1H, *H*–C(1)(Tx)), 7.85–7.71 (m, 4H), 7.64–7.55 (m, 4H), 7.42–7.37 (m, 1H, *H*-C(4)), 3.75–3.58 (m, 2H, C*H*$_2$O), 3.22–3.14 (m, 1H), 2.75–2.63 (m, 2H, TxC*H*$_2$-), 1.85–1.14 (m, 6H), 0.73 (s, 9H, ^{t}Bu), -0.13 (s, 3H, Si-C*H*$_3$), -0.16 (s, 3H, Si-C*H*$_3$).

5b: yellow oil; 22% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.45 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(8)(Tx)), 8.22 (d, *J* = 2.0 Hz, 1H, *H*–C(1)(Tx)), 7.83–7.70 (m, 4H), 7.63–7.53 (m, 4H), 7.45–7.40 (m, 1H, *H*-C(4)), 3.70 (dd, *J* = 9.8, 5.9 Hz, 1H, C*H*H'O), 3.63 (dd, *J* = 10.0, 7.1 Hz, 1H, CH*H'*O), 3.22–3.15 (m, 1H), 2.71 (t, *J* = 7.5 Hz, 2H, TxC*H*$_2$-), 1.85–1.20 (m, 8H), 0.68 (s, 9H, ^{t}Bu), -0.15 (s, 3H, Si-C*H*$_3$), -0.17 (s, 3H, Si-C*H*$_3$).

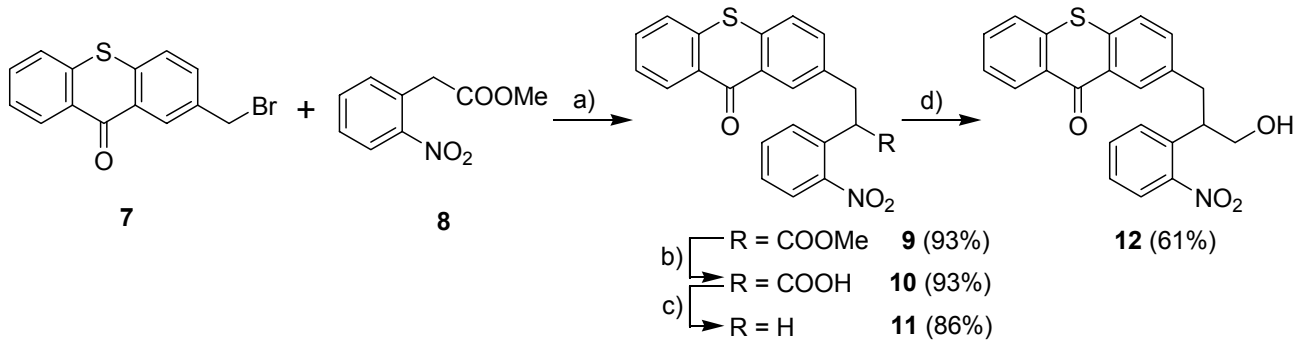
5c: yellow oil; 24% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.47 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(8)(Tx)), 8.27 (d, *J* = 1.7 Hz, 1H, *H*–C(1)(Tx)), 7.84–7.72 (m, 4H), 7.65–7.55 (m, 4H), 7.44–7.39 (m, 1H, *H*-C(4)), 3.73–3.60 (m, 2H, C*H*$_2$O), 3.16–3.09 (m, 1H), 2.70 (t, *J* = 7.6 Hz, 2H, TxC*H*$_2$-), 1.82–1.10 (m, 14H), 0.72 (s, 9H, ^{t}Bu), -0.13 (s, 3H, Si-C*H*$_3$), -0.15 (s, 3H, Si-C*H*$_3$).

Synthesis of **6a**, **6b**, **6c** (**T7S5-OH**, **T7S6-OH**, **T7S9-OH**). The TBDMS-protected alcohol **5a** – **5c** (8.86 mmol, 1 eq.) was dissolved in tech. THF (100 ml). At 0°C 1M TBAF-solution (11 ml, 11 mmol, 1.3 eq.) was slowly added and the solution stirred over night. Et_2O (100 ml), sat. NH_4Cl-solution (50 ml) and H_2O (50 ml) was added, and the organic layer was separated. The aq. phase was re-extracted with Et_2O (3 × 20 ml), the unified organic phases dried over $MgSO_4$ and the solvents evaporated. After column chromatography (silica gel, petrol ether-EtOAc-gradient) the product was obtained.

6a: yellow solid; 47% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.47 (dd, *J* = 8.1, 1.5 Hz, 1H, *H*–C(8)(Tx)), 8.25 (d, *J* = 2.0 Hz, 1H, *H*–C(1)(Tx)), 7.85–7.71 (m, 4H), 7.63–7.56 (m, 4H), 7.41–7.37 (m, 1H, *H*–C(4)), 4.71 (t, *J* = 5.3 Hz, 1H, O*H*), 3.57–3.47 (m, 2H, CH_2O), 3.12–3.05 (m, 1H), 2.74–2.63 (m, 2H, Tx–CH_2), 1.87–1.78 (m, 1H), 1.72–1.50 (m, 5H); EI-MS: molecular peak 433.1 (73%, theoretical mass 433.13), main fragment $(Tx–CH_2)^+$ 224.9 (100%).

6b: yellow solid; 53% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.47 (dd, *J* = 8.8, 1.3 Hz, 1H, *H*–C(8)(Tx)), 8.25 (d, *J* = 2.0 Hz, 1H, *H*–C(1)(Tx)), 7.86–7.71 (m, 4H), 7.65–7.55 (m, 4H), 7.43–7.38 (m, 1H, *H*–C(4)), 4.69 (t, *J* = 5.4 Hz, 1H, O*H*), 3.60–3.45 (m, 2H, CH_2O), 3.11–3.03 (m, 1H), 2.70 (t, *J* = 7.5 Hz, 2H, Tx–CH_2), 1.81–1.72 (m, 1H), 1.63–1.53 (m, 3H), 1.30–1.10 (m, 4H); EI-MS: molecular peak 447.0 (62%, theoretical mass 447.15), main fragment $(Tx–CH_2)^+$ 224.9 (100%).

6c: yellow solid; 32% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.47 (dd, *J* = 8.0, 1.5 Hz, 1H, *H*–C(8)(Tx)), 8.27 (d, *J* = 2.0 Hz, 1H, *H*–C(1)(Tx)), 7.85–7.72 (m, 4H), 7.65–7.54 (m, 4H), 7.44–7.39 (m, 1H, *H*–C(4)), 4.69 (t, *J* = 5.3 Hz, 1H, O*H*), 3.57–3.46 (m, 2H, CH_2O), 3.09–3.02 (m, 1H), 2.72 (t, *J* = 7.6 Hz, 2H, Tx–CH_2), 1.79–1.70 (m, 1H), 1.63–1.52 (m, 3H), 1.30–1.05 (m, 10H); EI-MS: molecular peak 489.2 (26%, theoretical mass 489.20), main fragment $(Tx–CH_2)^+$ 224.9 (100%).



Scheme S2: a) Methyl (2-nitrophenyl)acetate, KO^{t}Bu, THF, -78°C → r.t., 2 d; b) 1 M NaOH, r.t., 3 h; c) K_2CO_3, DMF, 50°C, 1 h; d) paraformaldehyde, KO^{t}Bu, DMSO, r.t, 12 h.

Synthesis of **9** (see also synthesis of **2a**, **2b**, **2c**). Methyl (2-nitrophenyl)acetate (5.80 g, 29.7 mmol) and 2-(bromomethyl)thioxanthone (8.95 g, 29.3 mmol) were dissolved in THF (150 mL) under N_2-atmosphere. KO^{t}Bu (3.88 g, 34.6 mmol) was added at -78°C. The blue suspension was left to warm to r.t. and stirred for 18 h. It was cooled to -78°C and sat. NH_4Cl-solution was added resulting in disappearance of the blue color. At r.t. CH_2Cl_2 (50 mL) was added and the organic phase separated (2 × with CH_2Cl_2), washed by water and dried over $MgSO_4$. The solvent was evaporated and the residue subjected to column chromatography (silica gel, petrol ether-EtOAc-gradient).

9: yellow foam; 93% yield; ^{1}H–NMR (400 MHz, $CDCl_3$): δ 8.60 (dd, *J* = 8.3, 1.0 Hz, 1H, *H*–C(8)(Tx)), 8.37 (d, *J* = 1.0 Hz, 1H, *H*–C(1)(Tx)), 7.88 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.64–7.39 (m, 8H), 4.59 (t, *J* = 7.7 Hz, 1H, C*H*COOMe), 3.64 (s, 3H, Me), 3.63 (dd, *J* = 13.9, 7.8 Hz, 1H, C*H*H'), 3.29 (dd, *J* = 13.9, 7.1 Hz, 1H, CH*H*').

Synthesis of **10**. The ester **9** (0.63 g, 1.5 mmol), 1,4-dioxane (12 ml) and 1 M NaOH (4 ml, 4 mmol) were stirred at r.t. for 3 h. The volume of the solution was reduced to about 20% to remove most of the dioxane. H_2O (20 ml) and 2 M HCl were added until the solution reached pH 2. The suspension was extracted with CH_2Cl_2 (5 × 20 ml), the unified organic phase was washed with NaCl-solution, dried over $MgSO_4$ and the solvent evaporated resulting in **10** as a yellow solid.

10: yellow solid, 93% yield, ^{1}H–NMR (400 MHz, DMSO–d_6): δ 12.79 (br. s, 1H, COO*H*), 8.44 (dd, *J* = 8.1, 1.0 Hz, 1H, *H*–C(8)(Tx)), 8.22 (d, *J* = 1.7 Hz, 1H, *H*–C(1)(Tx)), 7.88 (dd, *J* = 8.1, 1.0 Hz, 1H, *H*–C(3)), 7.83–7.55 (m, 7H), 7.49 (td, *J* = 7.7, 1.5 Hz, 1H, *H*–C(4)), 4.45 (t, *J* = 7.7 Hz, 1H), 3.58 (dd, *J* = 13.9, 7.3 Hz, 1H, Tx-C*H*H'), 3.26 (dd, *J* = 13.9, 8.1 Hz, 1H, Tx-CH*H*').

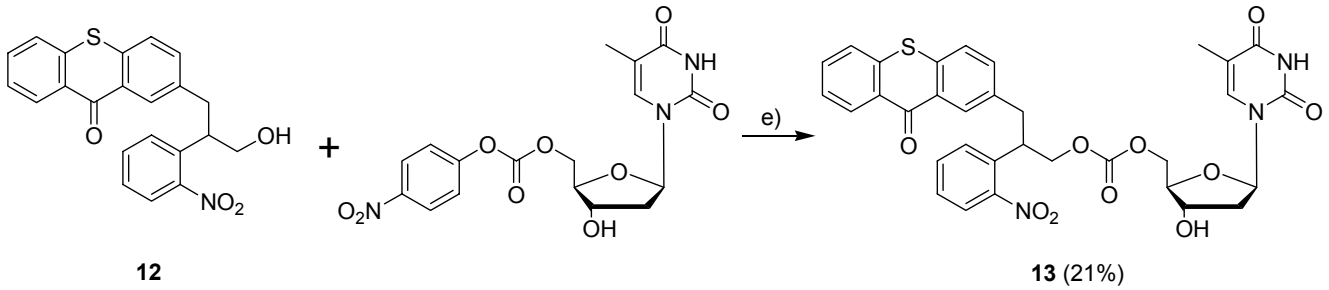
Synthesis of **11**. The carboxylic acid **10** (0.56 g, 1.4 mmol), K_2CO_3 (0.20 g, 1.45 mmol) and dry DMF (12 ml) were stirred at 50°C for 1 h. After cooling, the solution was poured into 0.1 M aq. HCl-solution (10 ml) resulting in the appearance of a yellow precipitate. The mixture was extracted with CH_2Cl_2 (3 × 20 ml), the unified organic phase was washed with sat. NaCl-solution, dried over $MgSO_4$ and the solvents evaporated. The product was separated by column chromatography (silica gel, petrol ether-EtOAc-gradient).

11: yellow solid; 86% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.46 (dd, *J* = 8.1, 1.5 Hz, 1H, *H*–C(8)(Tx)), 8.30 (d, *J* = 2.0 Hz, 1H, *H*–C(1)(Tx)), 7.95 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(3)), 7.84–7.74 (m, 3H), 7.67–7.54 (m, 4H), 7.48 (td, *J* = 7.6, 1.5 Hz, 1H, *H*–C(4)), 3.20–3.15 (m, 2H), 3.08–3.03 (m, 2H).

Synthesis of **12** (**T7S2-OH**). Compound **11** (0.51 g, 1.41 mmol) was dissolved in dry DMSO (50 ml) under N_2-atmosphere. Paraformaldehyde (0.085 g, 2.82 mmol CH_2O equivalents) and KO^{t}Bu (0.158 g, 1.41 mmol) were added and the suspension stirred over night. It was neutralized with sat. $NaHCO_3$ solution and extracted with CH_2Cl_2 (5 × 30 ml). The unified organic phase was washed with NH_4Cl-solution (1 × 30 ml) and H_2O (1 × 30 ml), dried over Na_2SO_4, and the solvent evaporated. The product was obtained after column chromatography (silica gel, petrol ether-EtOAc-gradient).

12: yellow solid; 61% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.44 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(8)(Tx)), 8.19 (d, *J* = 1.7 Hz, 1H, *H*–C(1)(Tx)), 7.83–7.64 (m, 6H), 7.57 (td, *J* = 7.5, 1.1 Hz, 1H), 7.49 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.40 (td, *J* = 7.6, 1.1 Hz, 1H), 4.91 (t, *J* = 5.2 Hz, 1H, O*H*), 3.67–3.63 (m, 2H, C*H*$_2$OH), 3.59–3.51 (m, 1H), 3.29 (dd, *J* = 13.7, 6.4 Hz, 1H, Tx-C*H*H'), 3.07 (dd, *J* = 13.7, 8.5 Hz, 1H,

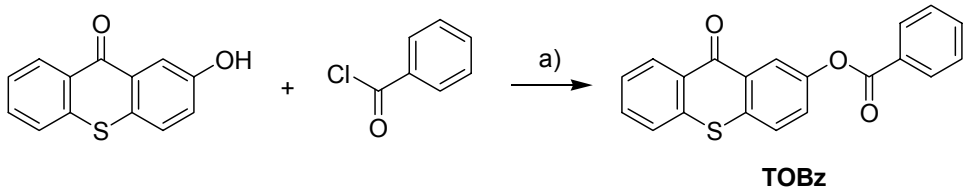
Tx-CH*H'*); EI-MS: (theoretical mass 391.1) molecular peak 391.2 (47%), main fragment $(Tx–CH_2)^+$ 225.0 (100%).



Scheme S3: e) pyridine, CH_2Cl_2, THF, DMAP, r.t., 2 d.

Synthesis of **13** (**T7S2-O(CO)Thy**). 4-Nitrophenyl thymidine-5-yl carbonate (0.69 g, 1.7 mmol)[4] was dissolved in dry pyridine (20 ml). **12** (1.11 g, 2.84 mmol) was dissolved in dry CH_2Cl_2 (10 ml), THF (5 ml) and DMAP (41 mg, 0.34 mmol), added to the pyridine solution and the mixture was stirred at r.t. for 2 d. H_2O was added and the mixture extracted with CH_2Cl_2 (3 × 20 ml). The unified organic phase was dried over $MgSO_4$ and the solvents evaporated. The residue was coevaporated with dry toluene (3 × 30 ml) to remove remaining pyridine. The product **13** was obtained after column chromatography (silica gel, CH_2Cl_2-MeOH-gradient).

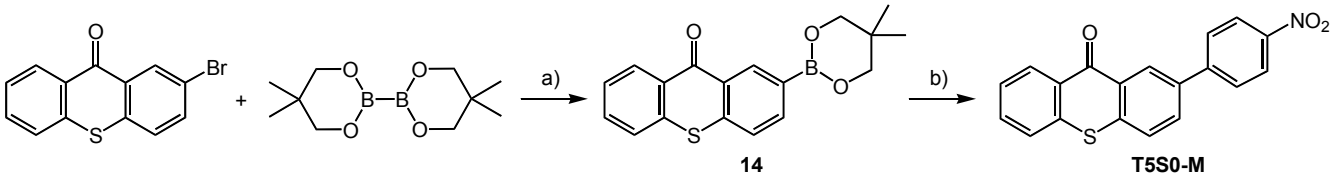
13: yellow solid; 21% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 11.26 (s, 1H, N*H*), 8.44 (d, *J* = 8.1 Hz, 1H, *H*–C(8)(Tx)), 8.20–8.18 (m, 1H, *H*–C(1)(Tx)), 7.89 (d, *J* = 8.2 Hz, 1H, *H*–C(5)(Tx)), 7.82–7.69 (m, 5H), 7.57 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51–7.34 (m, 3H, 2 aromatic *H* and *H*–C(5)(Thy)), 6.15 (td, *J* = 6.8, 2.7 Hz, 1H, *H*–C(1')), 4.49–4.40 (m, 2H, OCH_2), 4.27–4.13 (m, 3H, *H*–C(1') and 2 × *H*–C(5')), 3.91–3.83 (m, 2H, *H*–C(4') and benzylic C*H*), 3.31–3.25 (m, 1H, Tx-C*H*H'), 3.15 (dd, *J* = 13.7, 8.6 Hz, 1H, Tx-CH*H'*), 2.11–2.04 (m, 2H, 2 × *H*–C(2')), 1.69 (d, *J* = 2.5 Hz, 3H, Me); elemental analysis for $C_{33}H_{29}N_3O_{10}S \cdot 2\ H_2O$ (695.16 g/mol): calculated C 56.97 H 4.78 N 6.04, found C 56.89 H 4.85 N 6.13; FAB-MS (matrix 3-nitrobenzyl alcohol + NaI): 681.6 (M + Na^+, theoretical mass: 682.2).



Scheme S4: a) pyridine, 100°C, 40 min.

Synthesis of **TOBz**: Benzoyl chloride (0.66 g, 4.70 mmol) was added to a solution of 2-hydroxythioxanthone[5] (0.052 mg, 0.228 mmol) in pyridine (3 ml). Gradually, a colorless precipitate formed. After stirring at 100°C for 40 min the reaction mixture was poured onto ice water and acidified with 2M aq. HCl solution. It was extracted with CH_2Cl_2 (3 × 20 ml), the unified organic phase was neutralized with sat. aq. $NaHCO_3$ solution, washed with water and dried over MgSO4. After evaporation of the solvent, the product was purified by column chromatography (silica gel, petrol ether : EtOAc = 20 : 1).

TOBz: colorless solid; 66% yield; ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.49 (dd, *J* = 8.1, 1.2 Hz, 1H, *H*–C(8)(Tx)), 8.33 (d, *J* = 2.7 Hz, 1H, *H*–C(1)(Tx)), 8.22–8.17 (m, 2H), 8.00 (d, *J* = 8.8 Hz, 1H); 7.91–7.76 (m, 4H), 7.67–7.60 (m, 3H).



Scheme S5: a) Pd(dppf)Cl_2, KOAc, DMSO, 80°C, 4 h; b) 4-bromonitrobenzene, THF, H_2O, NaOH, Pd(dppf)Cl_2, 70°C, 12 h.

Synthesis of **14** (2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)-9H-thioxanthen-9-one): 2-Bromo-thioxanthone (694 mg, 2.38 mmol), bis(neopentylglycolato)diborone (577 mg, 2.55 mmol), potassium acetate (730 mg, 7.44 mmol) and Pd(dppf)Cl_2 (50 mg, 0.068 mmol, 3 mol%) were mixed together in

DMSO (20 ml) under N_2-atmosphere. The suspension was stirred for 4 h at 80°C. After cooling, CH_2Cl_2 (80 ml) and H_2O (100 ml) were added and the organic phase extracted. The water phase was extracted again with CH_2Cl_2 (2 × 30 ml). The unified organic phase was washed with sat. NH_4Cl–solution and dried over $MgSO_4$. The solvents were evaporated and the product purified by column chromatography (silica gel, petrol ether : EtOAc–gradient from 10:1 to 2:1)

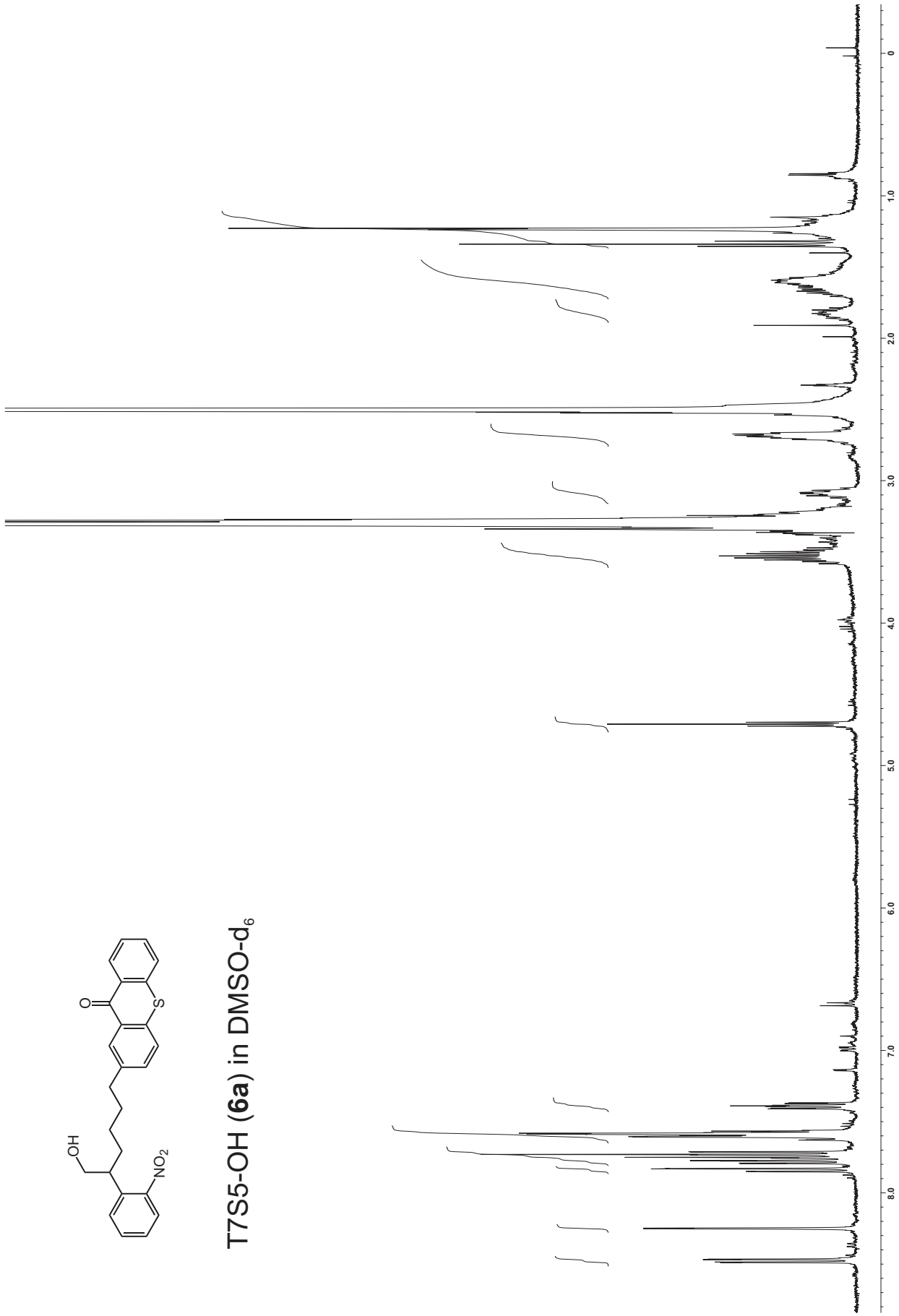
14: yellow solid, 85% yield, ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.81 (d, *J* = 0.8 Hz, 1H, *H*–C(1)(Tx)), 8.47 (dd, *J* = 8.1, 1.0 Hz, 1H, *H*–C(8)(Tx)), 7.97 (dd, *J* = 8.1, 1.5 Hz, 1H, *H*–C(3)(Tx)), 7.83 (d, *J* = 8.1 Hz, 1H, *H*–C(4)(Tx)), 7.78 (d, *J* = 8.1 Hz, 1H, *H*–C(5)(Tx)), 7.77 (td, *J* = 7.6, 1.5 Hz, 1H, *H*–C(6)(Tx)), 7.58 (td, *J* = 7.6, 1.2 Hz, 1H, *H*–C(7)(Tx)), 3.80 (s, 4H, 2 × C*H*$_2$), 0.97 (s, 6H, 2 × C*H*$_3$).

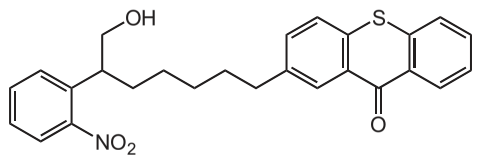
Synthesis of **T5S0-M**: The thioxanthyl boronic acid ester **14** (325 mg, 1.00 mmol) and 4-bromonitrobenzene 212 mg, 1.05 mmol) was dissolved in THF (20 ml) under N_2-atmosphere, and water (6 ml), NaOH (150 mg, 3.75 mmol) and Pd(dppf)Cl_2 (0.070 mg, 0.095 mmol, 9 mol-%) were added. After stirring for 12 h at 70°C and left cooling to r.t., the mixture was extracted with CH_2Cl_2 (2 × 20 ml), the unified organic phase washed with sat. NH_4Cl-solution, dried over $MgSO_4$, the solvent evaporated. The product was purified by column chromatography (silica gel, petrol ether : EtOAc–gradient from 10:1 to 1:1) and recrystallization from $CHCl_3$.

T5S0-M: yellow solid, 57% yield, ^{1}H–NMR (400 MHz, DMSO–d_6): δ 8.80 (d, *J* = 2.2 Hz, 1H, *H*–C(1)(Tx)), 8.52 (dd, *J* = 7.9, 1.1 Hz, 1H, *H*–C(8)(Tx)), 8.36–8.32 (m, 2H, AA'-part of the AA'MM'-system of nitrophenyl), 8.09–8.05 (m, 2H, MM'-part of the AA'MM'-system of nitrophenyl), 8.17 (dd, *J* = 8.3, 2.2 Hz, 1H, *H*–C(3)(Tx)), 7.79 (d, *J* = 8.5 Hz, 1H, *H*–C(4)(Tx)), 8.86–7.77 (m, 2H, *H*–C(5)(Tx) und *H*–C(6)(Tx)), 7.62 (td, *J* = 7.4, 1.5 Hz, 1H, *H*–C(7)(Tx)).

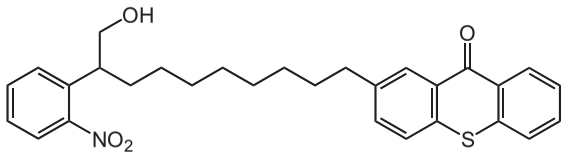
Elemental analysis, melting points. Elemental analyses were performed by the microanalytical laboratory of the University of Konstanz. The uncorrected melting points were measured on a B454 melting point apparatus from Büchi.

4. NMR spectra

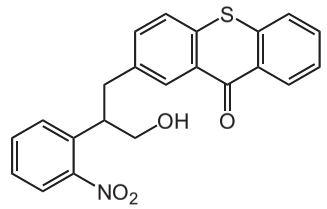




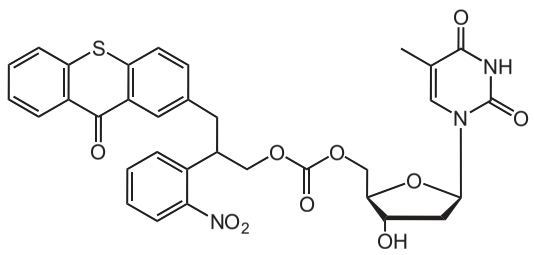
T7S6-OH (**6b**) in DMSO-d_6



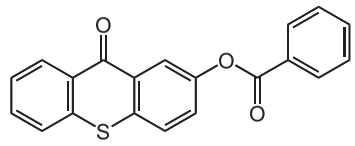
T7S9-OH (**6c**) in DMSO-d_6



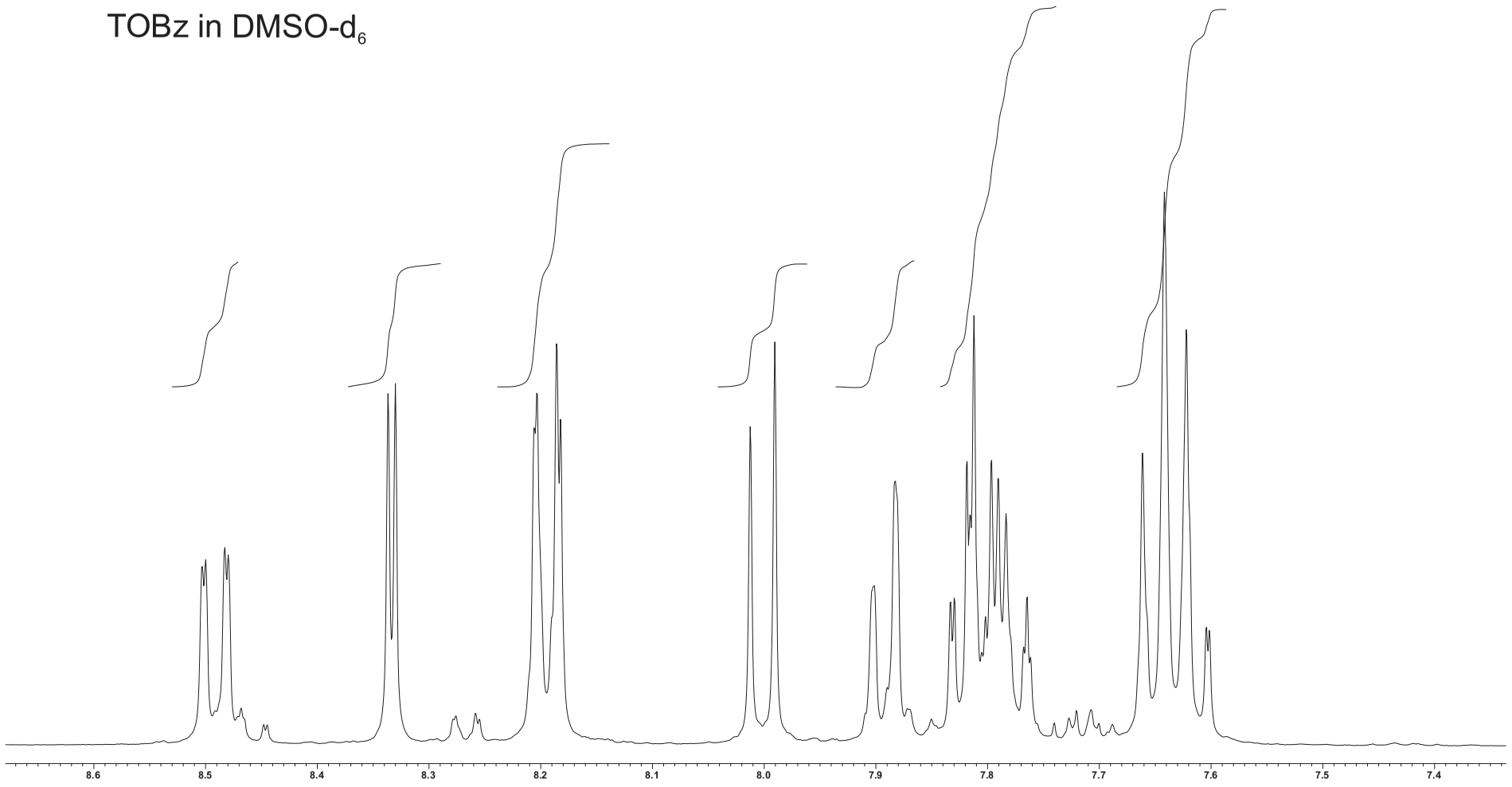
T7S2-OH (**12**) in DMSO-d_6

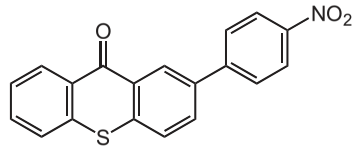


T7S2-O(CO)Thy (**13**) in DMSO-d_6

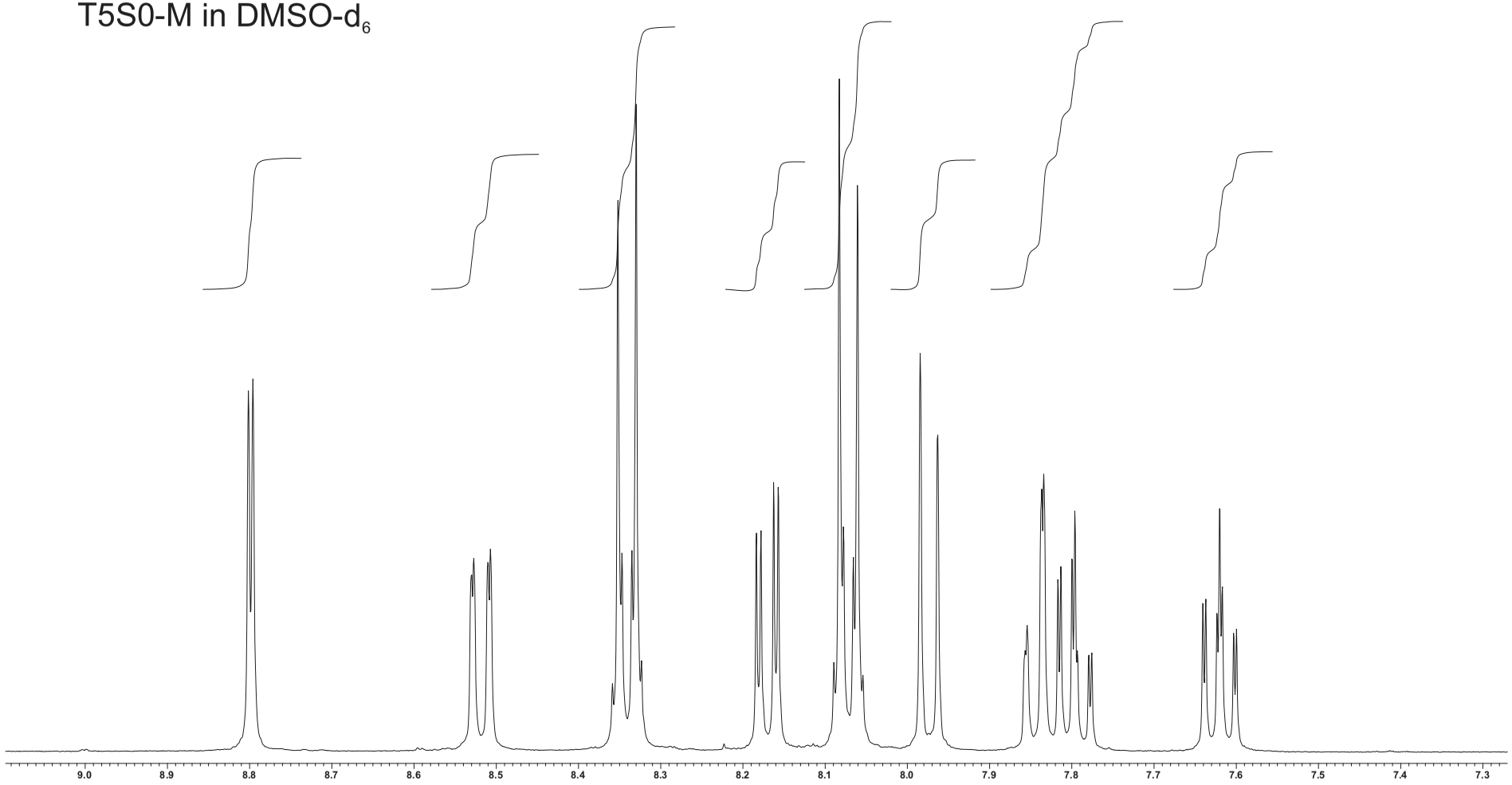


TOBz in DMSO-d_6





T5S0-M in DMSO-d_6



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